

BLISTERING OF GRAPHITE/POLYMER COMPOSITES
GALVANICALLY COUPLED WITH METALS IN SEA WATER

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CONTENTS

ABSTRACT.....	1
Introduction.....	2
Composites Studied.....	2
The Morphology of Galvanically Induced Blisters in Carbon	
Fiber Composites.....	3
Blister Fluid Analysis.....	4
Electrochemical Studies	7
MECHANISM OF GALVANIC BLISTERING.....	9
References	13

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Blistering of Graphite/Polymer Composites Galvanically Coupled to Metals in Seawater

ABSTRACT

Carbon reinforced polymer composites are extensively used in aerospace and marine applications. Carbon fibers in carbon reinforced composites, being electrically conductive, form galvanic couples when they come into contact with most metals in the presence of an electrolyte. Carbon is a noble material and becomes a cathode in the galvanic couples with steel, aluminum, etc. The galvanic couple resulted in blistering of these composites whereas uncoupled samples did not show blisters even after exposure to electrolyte for two years. These blisters termed as "galvanic blisters" are filled with liquids with pH 14. Galvanic blisters initiate at the fiber/matrix interface. During this research, several carbon composites with vinyl ester, polyester, epoxy matrices were found to blister galvanically. Experiments showed that while fiber surface treatments may aid this blistering, they do not play a necessary part in blister formation.

Electrochemical studies indicated that oxygen reduction takes place on the carbon surface in carbon fiber composites. The current is found to be limited by diffusion of oxygen to the cathode site.

The blister liquids from carbon composites and polymer coated silver were analyzed. A mechanism for galvanic blistering is proposed based on these results. According to this mechanism, galvanic coupling produces a surface charge on the conductive fibers which results in modification of the polymer/fiber bonding. This occurs if the polymer is saturated with water and ions and is independent of the polymer composition. This makes possible a water clustering at the interface which starts the delamination process. In an aerated environment, the oxygen reduction that takes place at these zones produces hydroxyl ions and a sodium hydroxide solution is formed. The sodium hydroxide solution creates an osmotic pressure which causes the blister to grow. In some polymers, the latter step can be exacerbated by polymer breakdown.

Introduction:

Carbon fibers being electrically conductive pose an entirely new mechanism for degradation in carbon reinforced polymer composites. Carbon is a very noble material and induces corrosion of most of the metals that are galvanically coupled to it. This phenomenon has a high degree of probability in marine environments. The galvanic coupling of carbon reinforced composites to metals, besides resulting in enhanced metallic corrosion also was found to degrade the polymer composite itself. The galvanic degradation of the composite is not limited to one polymer system. Tucker and Brown¹ observed blistering of carbon fiber/vinyl ester composites galvanically coupled to steel and aluminum alloys in seawater. Donnellen and Cochran² studied the galvanic degradation of polyimide composites and Sloan³ studied that of graphite epoxy composites. A common feature in all these cases was that the degradation occurs under galvanic coupling conditions with a high pH fluid filling the blister cavities. A very limited amount of work exists on the degradation of polymer composites by galvanic interaction.

The objective of the present research program is to conduct analytical and experimental investigations that shall lead to the complete characterization of the electrochemically driven degradation in these composites.

Composites Studied:

1. Vinyl ester (Derakane 470-36) with T300 unidirectional fibers with fiberglass wefts in cross weave.
2. Vinyl ester with a graphite disc.
3. Vinyl ester over glassy carbon.
4. Vinyl ester over silver.
5. Vinyl ester with T 300 mat.
6. Epoxy resin with T300 mat

The Morphology of Galvanically Induced Blisters in Carbon Fiber Composites:

As various blistered samples became available during this past year extensive thin section and polished section microscopy was performed to determine the nature, position and shape of the blisters. Our observations confirmed most of the conclusions presented last year and show added evidence to support the galvanic growth model.

As reported last year, the vinyl ester-fiber composite exposed to sea water does not blister after 2 years but if the same sample is coupled to steel or has a voltage impressed on it using a platinum counter electrode, blister in the order of a micron in diameter form on the near surface filaments after two hours. Because of the thin overlaying layer of polymer these blisters break open after approximately 1 day and expose the outer filaments to the electrolyte solution and after 2 to 3 days, larger blisters nucleate on the surface filament tows at the trough of the sinusoidal wave caused by the weave texture.

Figure [1] shows a cross-section view through a typical blister. A magnified view of the same blister cavity is shown in figure [2]. The black line which extends across the field of view in the gap between the vinyl ester of the composite and the overlying mounting medium. The width of the elliptical filament is 1mm. The blister roof at this cross-section is approximately 0.1mm thick and has thinned at the crest by creep induced by the internal pressure in the blister cavity. In subsequent sections, the blister closes as the tow rises toward the surface and as the tow goes deeper and under the glass weft the blister will stay adjacent to the carbon filament and go under the bundle of glass filament which cross the tow. Such a relationship is shown in figure [3] with the blister cavity between the carbon and the glass. After these larger blisters emerge from under the glass the blister cavity opens again and is identical to that shown in figure [1].

In last year's report evidence was presented to suggest that the blisters formed with in the tow, under the first few layers of filaments. As shown by these micrographs and many other observations, the blisters form at the carbon-filament tow/vinyl ester interface. While some fibers are ripped off the tow by adhesion to the separating polymer, almost all of the fibers are on the bottom of the blister and the polymers on the roof is clearly separated at the interface. The ripped off fibers are those suspended in the cavity in figure [2].

Another feature observed is the convergent growth of two or three blisters into one larger blister. This feature is shown in figure [4].

No blister has ever been observed inside one of the tows. Furthermore, no blisters have been observed on any surface other then the outward facing near surface tows.

Blisters do not form on the bottom of the surface tows or on any tow inside the composite under the surface layers.

It has been argued that blister related debonding of the polymer filament interface might take place inside the composite but that the internal pressure would not be great enough to cause deformation of the overlying fiber reinforced polymer. However, examination of many thin sections and polished sections failed to show any such separations at filament matrix interfaces.

Our conductance experiments show that all filaments have point contacts with other filaments in their own tow and that each tow contacts many other tows so that electrical conductivity is complete and when galvanically coupled there is an equipotential charge distribution through out the composite. Therefore the occurrence of all blisters on near surface tows suggest diffusion of a species into the composite from outside controls blister location. Cathodic oxygen reduction would explain the position. The diffusing oxygen molecules are depleted at the new surface fibers and the partial pressure of oxygen inside the composite is kept low and therefore no internal blisters can form.

Blister Fluid Analysis:

Introduction

For all the composites employed in the second year, blisters nucleated and grew on coupled samples. This suggests that the primary requirement for the composite to be susceptible to galvanic blistering is that it contain a conductive element within the polymer. It was thought at one time that the glass fibers in the composite were important to the blistering reaction. It may be that they localize blister initiation by providing a specific initiation site but are not necessary, as blisters were found in silver/vinyl ester and graphite-disk/vinyl ester composites. This suggests that the components which fill the blister with fluid are therefore available within the polymer or alternatively available from the electrolyte or are available from products of the electrochemical reactions occurring. A crucial set of experiments is therefore identification of blister fluid to determine the source of the blister fluid. This in turn will provide information on the necessary mechanistic components.

Details of Analysis

Fluid from blisters in the vinyl ester based composites including the silver composite were analyzed by size exclusion chromatography/high performance liquid chromatography (SEC/HPLC), fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM) using techniques developed during this study.

The SEC/HPLC technique was used to separate and detect the number of components present and to identify their molecular weights by suitable calibration. A Waters HPLC unit coupled to a Waters Differential Refractometer detector was employed. The column used was a Waters Ultrahydrogel™ column packed with polymethylmethacrylate gel. This column is compatible with aqueous solutions in the pH range of 2 to 12. The column can effectively separate molecules within the range of 100 to 2000 molecular weight (based on polyethylene glycol standards). Results from HPLC analysis showed that there is no water soluble component in the vinyl ester resin except for a little solubility of monomer itself (about 1500 Mwt.). The HPLC runs of blister fluids did not show any such high molecular weight species. This indicates that there are no leach products from the polymer matrix which could enter the blister fluid. This was also supported by the fact that no peaks within the ranges characteristic of carbon-carbon bond vibrations were found in the IR spectra of the blister fluid samples from graphite disk and silver composites. However, in the previous year's report, it was mentioned that the vinyl ester coating on a Platinum cathode degraded under galvanic coupling conditions. It occurred because the vinyl ester on platinum was not completely crosslinked as its surface was exposed to air and it lost most of the styrene. This resulted in incomplete crosslinking and made the film susceptible to attack by high pH solution.

Transmission electron microscopy of the blister fluid from the vinyl ester based composites after it was dried was conducted in order to check the morphology and composition of any solid products formed. The photomicrograph of figure [5] shows the galvanic blister fluid precipitates from silver/vinyl ester cathode. The visual evidence from this micrograph suggests one single phase constituting the blister precipitate. These precipitates are crystalline as characterized by strong electron diffraction pattern. X-ray dispersive analysis of these crystals showed the elements C, Na and O. It was thought that these crystals could be sodium carbonate. To check this, the FTIR spectrum of these precipitates shown in Figure [6] was compared with the FTIR spectrum of sodium carbonate crystals shown in figure [7]. The two spectra are identical producing peaks at 1425 cm^{-1} and it was concluded that indeed these crystals are sodium carbonates. *Thus, an aqueous solution (also detected by FTIR) of sodium hydroxide and sodium carbonate essentially constitutes the galvanic blister fluids in the vinyl ester coated silver cathode and*

in vinyl ester coated graphite cathode (by a similar analysis). However, the surface treatments of carbon fibers may bring in more components into the blister fluids from carbon fiber/vinyl ester composites whose analysis is discussed next.

Photomicrographs shown in figure [8] and [9] show the two distinctly different phases in the precipitates of the blister fluids from carbon fiber/vinyl ester composite. The amorphous (indicated by electron diffraction study), gel like material in figure [8] showed the elements Na, O and Si determined by X-ray dispersive analysis. This might be sodium silicate or *water glass* which is extremely hygroscopic. The sodium silicate could be from the interaction of silane coating of the fibers (which the manufacturer used to ensure good bonding between glass fibers and the polymer) with the high pH blister fluid because no sodium silicate was found in the blister fluid precipitates of silver/vinyl ester composite. Figure [9] shows the other phase which produced a strong electron diffraction pattern indicating it is crystalline. The elemental analysis showed C, Na, O and S. Some of these crystals must be sodium carbonate crystals besides some sulfur containing crystals. It was thought that the sulfur containing crystals could be a sulfate. However, the corresponding FTIR spectrum for this blister fluid precipitates (figure [10]) showed no absorbance peaks characteristic of bond stretches of any sulfur containing group which must appear around 1000 cm^{-1} - 1200 cm^{-1} . Similarly, no peak corresponding to a silicate ion around 1000 cm^{-1} is present. However, the source of sulfur and silicon in whatever form they are present, must be from the fiber surface treatments since they are absent in the blister fluids from the silver/VE and graphite-disk/VE composites. The reason for these groups not appearing in FTIR spectra may be due to their low concentrations in the blister fluid solution. *The carbonate peak at 1425 cm^{-1} can be seen indicating the presence of sodium carbonate.* The spectrum also shows a peak at 1555 cm^{-1} which is absent in the spectra of blister fluid precipitates of silver/vinyl ester and graphite disk/vinyl ester systems. This peak which corresponds to OH bending vibrations of water could be due to presence of little water in the blister precipitate as sodium silicate is highly hygroscopic.

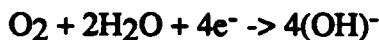
The source of sodium carbonate was identified to be the dissolved carbon dioxide in the form of carbonic acid (H_2CO_3) in the electrolyte solution which will be neutralized by the highly basic sodium hydroxide solution formed at the cathode. This is discussed in more detail in the section 'theory of galvanic blistering'.

In conclusion, the essential constituents in a galvanic blister are sodium hydroxide and sodium carbonate. In the case of carbon fiber composites some other compounds or complexes may appear in the galvanic blisters due to their fiber surface treatments which may or may not affect the blister formation and growth.

Electrochemical Studies:

The Cathodic Reaction

The knowledge of the cathodic reaction on a cathodic surface under a polymer film is imperative to understanding of nature of the electrochemical blistering. The cathodic reaction on most of the carbon surfaces and noble metals in a near neutral or basic environments is the reduction of oxygen to hydroxyl ions⁴. The reaction proceeds as follows:



However, whether this reaction occurs on a cathode surface surrounded by a polymer film has yet to be determined. Experiments were conducted to obtain current values for various cathode potentials for both carbon/vinyl ester composite and carbon fiber mat⁵. The curves are shown in Figure [11]. The curve for free fibers is typical for cathodic reduction of oxygen on carbon surfaces⁴. The range of potential over which the current becomes almost independent of potential is the diffusion controlled region where the rate of cathodic reaction is limited by the diffusion of oxygen towards the electrode: The curves for both composite and the fibers are very similar indicating that O₂ reduction is the predominant reaction taking place at the polymer/fiber interface in the composite. However, the galvanic current is lower for the composite than for the carbon fibers by about two orders of magnitude. The current profile for the case of this composite is not only indicative of an increased activation energy for the cathodic reaction under the polymer film but also suggests lowered diffusion rates of oxygen towards the cathode. The apparent increase in activation energy for the composite could be due to the reduction in the number of available active sites on cathode surface for the cathodic reaction due to the presence of polymer adhesive bonds with the cathode surface.

The plot in Figure [12] shows the blister initiation time versus current density in carbon/vinyl ester composite. The current values noted after three days of exposure are presented. These values are considered because these are the currents which are expected to cause composite blistering to begin with. The data points represented by filled characters are the currents from samples of experiments terminated prematurely due to short circuit. However, these values are presented to show reproducibility of current data between different samples. The plot reveals that the damage to the composite in the form of

blistering is very sensitive to even small differences in the current densities. However, this will be less intriguing if one realizes that galvanic blistering itself can occur even due to very small current densities.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy, a relatively new but powerful technique widely applied to characterization of protective coatings on metals^{6,7}, has already proven to be effective for the quantitative electrochemical studies of carbon composites. This technique was applied to study effects of long term exposure of carbon composite cathodes when they form blisters. Disc samples 6cm in diameter were sectioned from a sheet of carbon fiber vinyl ester composite. These were then placed with the resin rich surface exposed to electrolyte (3% NaCl solution). The exposure area was 5 sq. cm. The potentials were measured against a standard calomel electrode with a platinum wire as the counter electrode.

The principle behind this quantitative electrochemical study is to impress a small, sinusoidal signal of about 5 mV amplitude over the DC potential of the sample and record the response impedance. The impedance changes are as a result of the various electrochemical changes near the cathode. A proper modelling of the data using a model electrical circuit which represents the physical situation at hand would tell which parameter is more influential and also about the temporal changes of the electrochemical history of the sample. An EG&G PARC model 273 potentiostat and a Solartron 1255 HF frequency response analyzer were used. The frequency response analyzer supplies the required ac signal and analyzes the response signal from the sample. The instruments were coordinated and the data was acquired using an IBM personal computer. Impedance data was collected at various time intervals.

The model used to fit the impedance data is shown in figure [13]⁸. It consists of a charge transfer resistance in parallel with a constant phase element which is in series with a pore resistance in parallel with a second phase element which in turn is in series with the solution resistance of the electrolyte. This circuit is commonly used for polymer films over metals⁷. However a distinct difference is that for composites the charge transfer resistance is for a cathodic reaction while for polymer coated metal films the anodic oxidation charge transfer resistance is often considered. The pore resistance data for several potentials as a function of exposure time is shown in figure [14]. The pore resistance which represents the regions of exposed fiber to the electrolyte. The rapid decrease in pore resistance indicates (1) the rupture of several small blisters which form on the fibers closest to the surface,

exposing these fibers to the electrolyte and (2) cathodic delamination which will increase the area of exposure. Thus, the drop in pore resistance is very indicative of the initiation of blisters. It can be seen that the resistance drops by about 4 orders of magnitude under applied potential conditions whereas the drop is just about an order of magnitude under open circuit conditions. Moreover, the pore resistance value does not change much after long periods of exposure. It was thought that variations in polymer capacitance would directly reflect any changes in polymer geometry (deformation) or its state. More work is required in this direction since this knowledge will help in monitoring blister formation.

PROPOSED MECHANISM OF GALVANIC BLISTERING

Theory of Galvanic Blistering

In each section of this report, conclusions were drawn based on the experiments discussed. The basic sections, nucleation, and growth of blisters on carbon composites, blister formation on various cathodes, impedance studies and blister fluid analysis, each resulted in conclusions regarding the mechanism of galvanic blistering. In this section the results are drawn together to form a theory for galvanic blistering. The steps which lead to blister formation are listed below and described in the following section:

1. Components of the composites.
2. Diffusion of water and oxygen into polymer matrix.
3. Diffusion of ions to convert polymer to a solid electrolyte.
4. Charging of carbon filaments.
5. Debonding of polymer and formation of a Helmholtz water layer.
6. Reduction of oxygen. (other ions Cu_{++} , H^+)
7. Increased concentration of NaOH .
8. Osmotic pressure build up.
9. Creep of polymer and growth of blister.

1. Components of the Composite: The composite must have an electron conducting component which in this case is conductive carbon fibers. Before the composite is formed the carbon fibers are treated to form functional groups such as acid groups, sulfates and

chromates to assure interaction with polymer matrix⁹. These groups can be hydrolysed to aid in blister growth at a later stage. Some sulfur containing groups are found in blister solutions.

2. Diffusion of water and oxygen into the polymer matrix: Upon immersion of the composite, water diffuses into the polymer matrix. The non-ionic species such as oxygen molecules will also diffuse. The diffusion rate and amount will depend on the partial pressure of oxygen around the composite and the temperature.

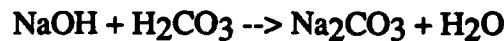
3. Diffusion of ions and the formation of the polymer solid electrolyte: The diffusion of ions in dry polymers is extremely slow because of their low dielectric constants. As the polymer absorbs water into its structure, the diffusion coefficient for ions increases by orders of magnitude. The solvated ion can now move in response to a charge on the fibers and the solid polymer insulator has become a solid electrolyte and can serve to complete an electrochemical circuit.

4. Charging of filaments: Either by joining the composite to a less noble metal (by bolting, clamping, press fitting, etc.) or by imposing a cathodic current on the composite, the fibers (which contact each other throughout the composite) become electron-rich, negatively charged cathodes. Depending upon the magnitude of the charge (voltage difference between electrodes) the adjacent polymer will respond by polarization to give an induced dielectric charge and the positively charged ions, (Na^+) will begin to move toward the filament¹⁰.

5. Debonding of the Polymer and Formation of Helmholtz Water layer: Zone of the cross-linked polymer which are electron-rich will undergo an entropy change as they rotate or shift away from the charged fiber surface. This will increase the free volume at the polymer/carbon surface. Also, electron-poor units of the polymer will move forward the fiber. Water molecules which have uniformly saturated the polymer can enter the free volume with their positive dipole ends along the fiber surface. The formation of this Helmholtz layer, which can be several layers thick, represents the nucleation of a new phase in the composite - a dish shaped droplet of water. Sodium ions will be drawn into this droplet (with dragged chloride ions preventing a space charge build-up) and the water droplets becomes a unit of sodium chloride solution. Similarly, protons associated with the HCO_3^- ions (from dissolved CO_2) will also be drawn into the solution. The sodium will be kept away from the surface by the polarized water.

6. Reduction of Oxygen: While the events are penecontemporaneous, oxygen molecules dissolved in the water saturated polymer can now transfer to the solution and , since they are not charged, they can penetrate the Helmholtz layer, accept an electron and react with water to form OH^- ions. There are other ions which can fulfill the role of electron environment. The reduction of copper ion, especially in sea water where the composite could be painted with a copper releasing antibonding paint, will take place at about the same potential. Hydrogen production by water electrolysis will take place at higher potentials.

7. Increase Concentration of NaOH:The build up of hydroxyls displace chloride ion from sodium ions and draw more sodium into the solution at the fiber surface. The pH shifts to 14 and the solution becomes more concentrated. The potential and the oxygen partial pressure will determine the rate of OH^- production. It diffuses out of the solution and through the polymer to the sea water but if it is produced faster than it diffuses, the solution concentration builds. Besides, some of the sodium hydroxide formed will be neutralized by the H_2CO_3 present to form sodium carbonate according to:



8. Osmotic pressure build up: Any two solutions separated by a permeable membrane which have different concentrations of ions or soluble molecules have a free energy difference. The equilibrium driving force will activate a diffusion process which will operate until the energy difference is zero. In sea water, the concentration outside the composite is about 0.05 molar. The sodium hydroxide solution is originally several molar. Water will be drawn into the solution at the fiber surface creating an osmotic pressure inside the solution. As the amount of inner solution grows by dilution the pressure will build until it is great enough to oppose the osmotic diffusion. When the pressure is great enough to break the bonds between the polymer and the fibers the blister cavity begins to open. Pressure drops, and a new diffusion event can begin.

9. Creep of the Polymer and Blister Growth: The blister cavity can grow by creep of the polymer as well as interface cracking. The blisters that form very close to the composite surface will split open in several hours because of the thinness of the blister roof. Upon braking, the carbon fibers are exposed to the solution and keep the oxygen partial pressure low in the area surrounding the exposed spot. This protects the immediate vicinity from

further blistering and the second generation of blister is always at a finite distance from the exposed carbon fibers.

The blister initiation times and the growth rate are a function of the following variables:

- V- conductivity of carbon fibers
- l- polymer thickness over the carbon fibers
- D₁- diffusion coefficients of species towards cathode through polymer
- e- dielectric constant of the polymer
- ø- potential difference between the carbon fibers and the anodic material
- d- thickness of Helmholtz layer
- K- charge transfer coefficient
- P_{O₂}- partial pressure of oxygen in the system
- C- concentration of salt solution (and other ions which may be present).
- T- temperature
- D₂- diffusion coefficients of species away from cathode through polymer
- E- modulus of polymer
- c- creep properties
- s- tensile strength of polymer
- t- time elapsed after connecting composite to less noble metal

Many of these variables change with time during the blistering process. How they change and the interactions of one variable upon another, while understood, in a qualitative way is the basis for continuing study which ideally will culminate in a predictive model for blistering.

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Figure 1. Blister opening in carbon/glass/vinyl ester composite



Figure 2. Enlarged view of blister opening in carbon/glass/ester/vinyl ester composite



Figure 3. Micrograph revealing blister opening passing under the glass tow



Figure 4. Micrograph showing two blisters merging into one



Figure 5. Blister fluid precipitates from silver/vinyl ester composite

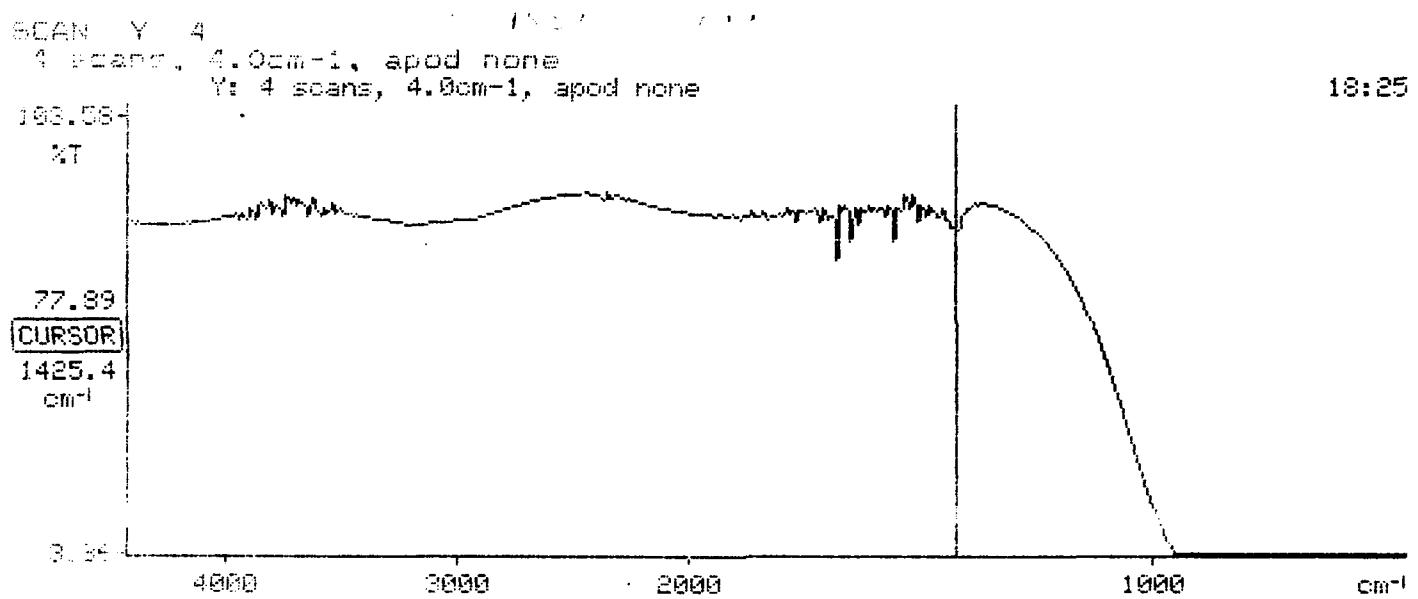


Figure 6. FTIR spectrum of blister fluid precipitates from silver/vinyl ester composite

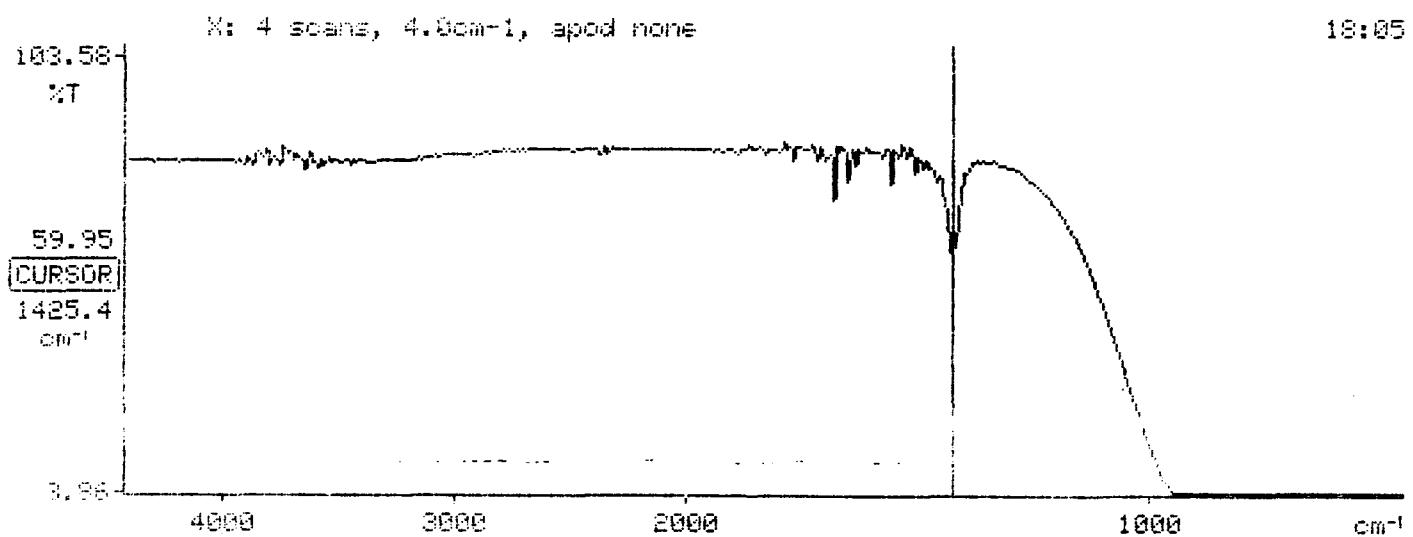


Figure 7. FTIR spectrum of sodium carbonate crystals



Figure 8. Amorphous substance found in blister fluid precipitates from carbon/glass/vinyl ester composite



7830 80.0KV X40K 200nm

Figure 9. Crystalline substance found in precipitates from carbon/glass/vinyl ester composite



Figure 10. FTIR spectrum of blister fluid precipitates from carbon/glass/vinyl ester composite

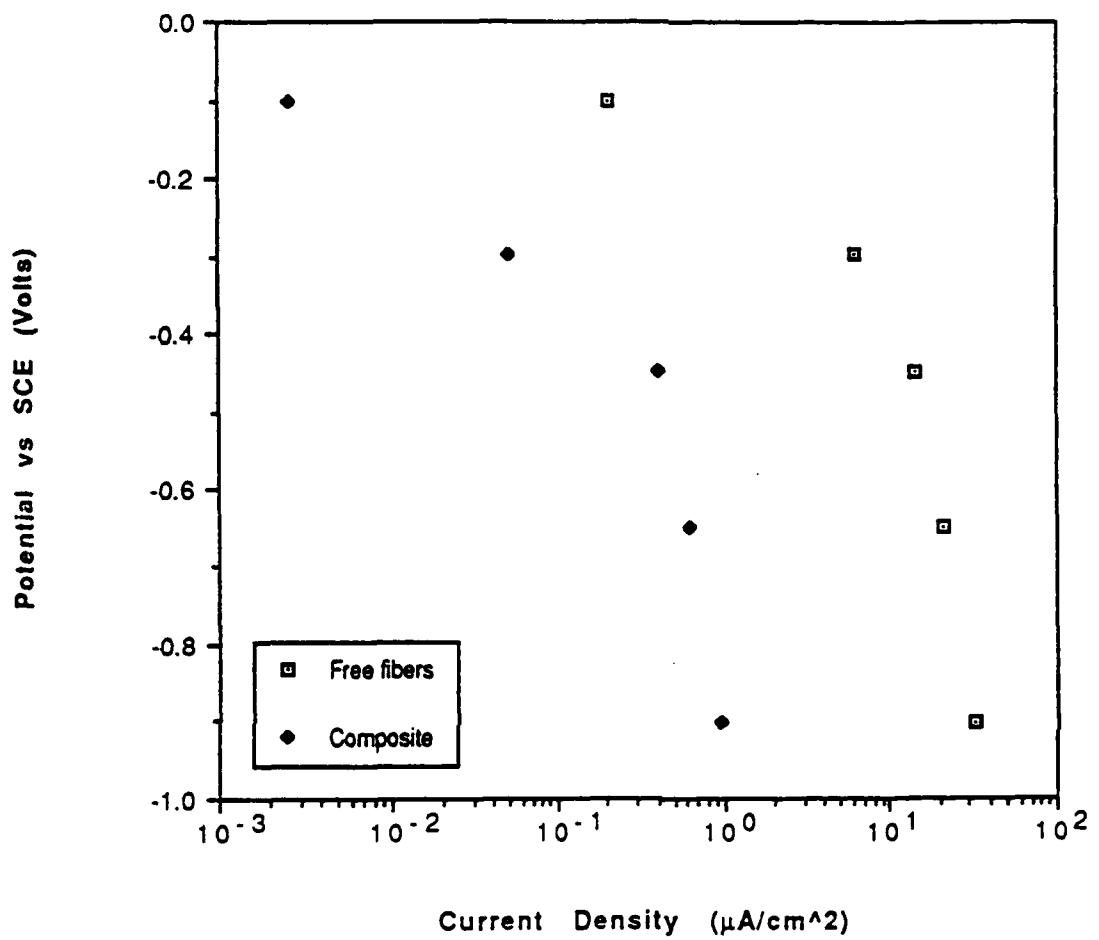


Figure 11. Cathodic potential versus current density curves for free carbon fibers and carbon fiber/vinyl ester composite

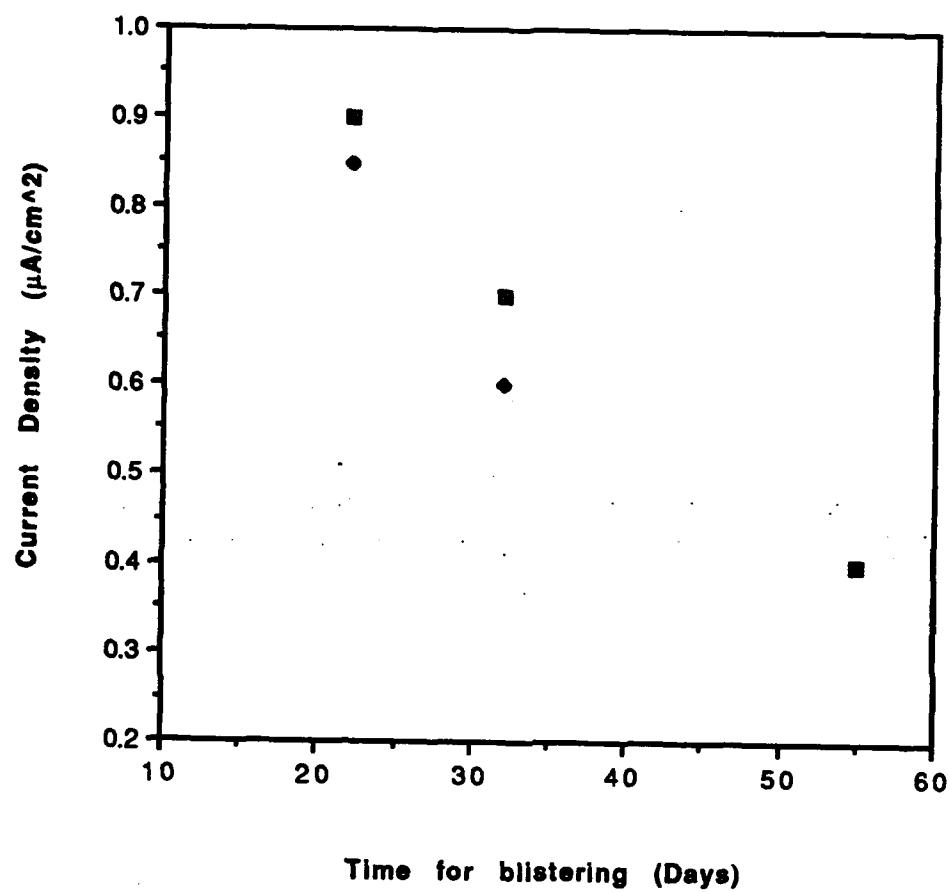


Figure 12. Current density versus blister initiation time for the carbon/vinyl ester composite

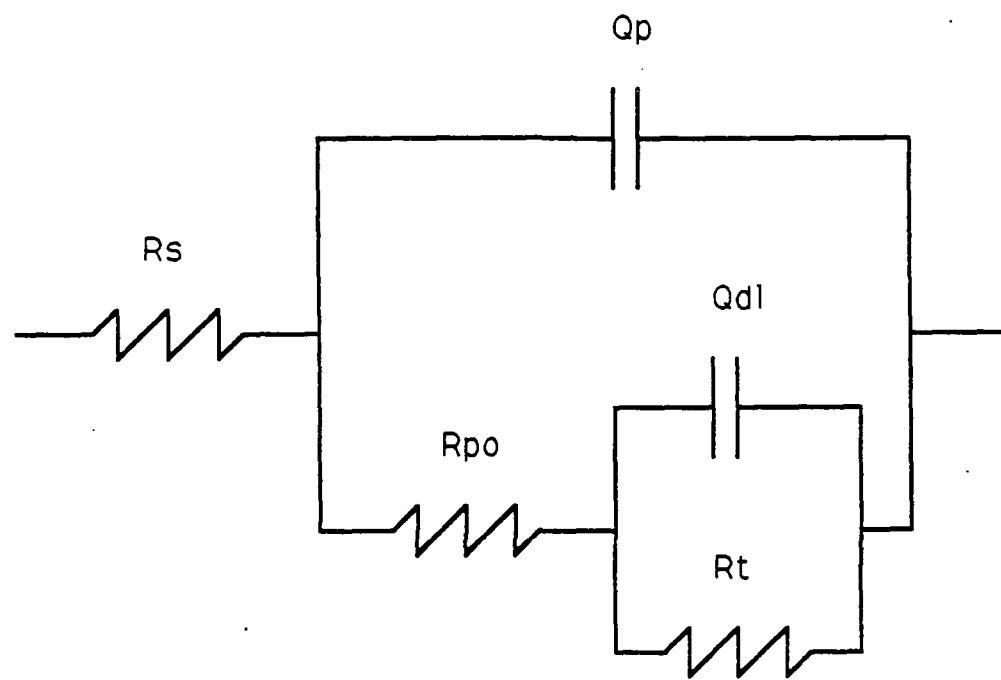


Figure 13. Equivalent circuit model used for modelling of impedance data from carbon fiber/vinyl ester composite

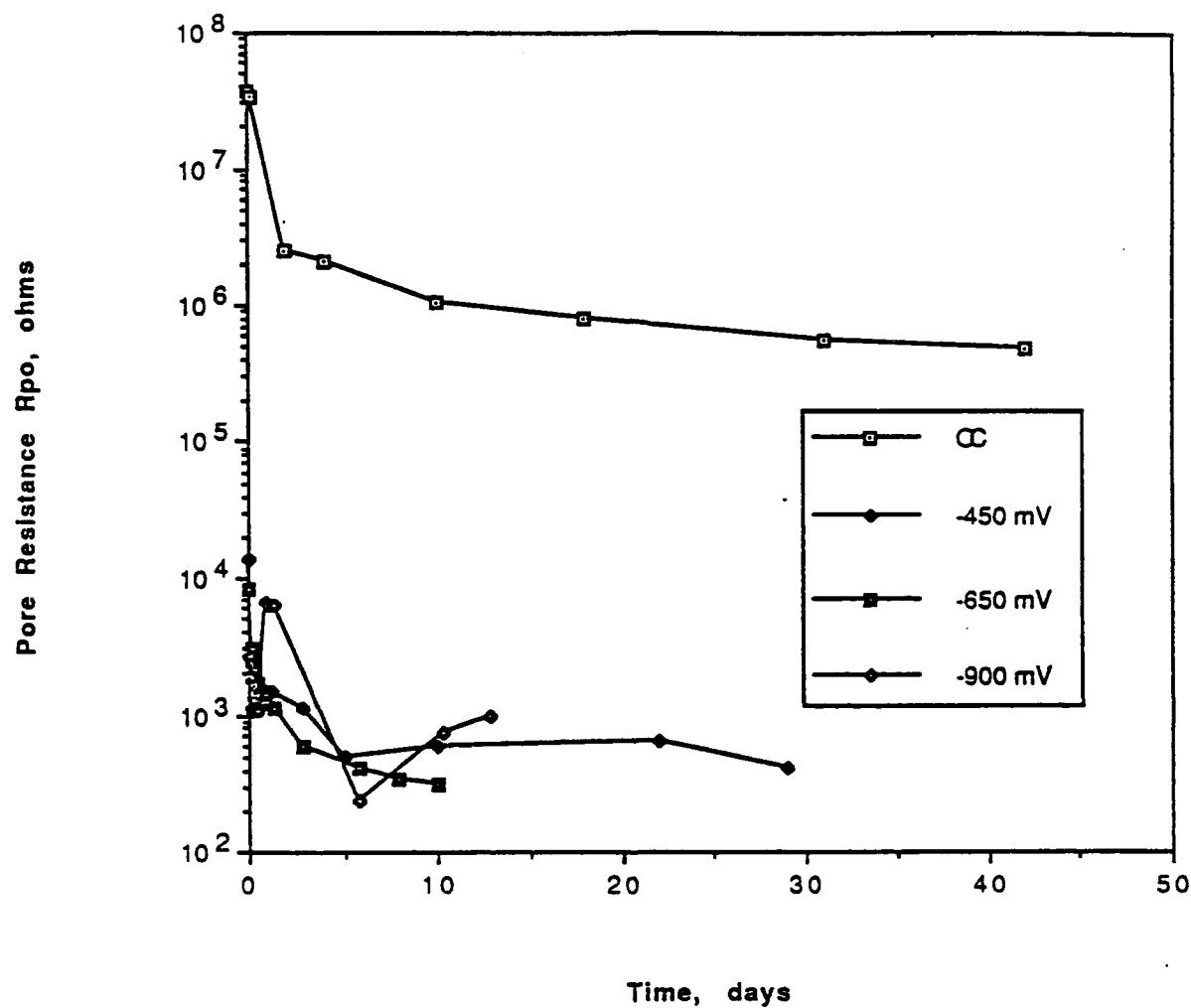


Figure 14. Temporal pore resistance variations in carbon/vinyl ester composite at different applied cathodic potentials for long term exposure